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[Document Name] Description

[Title of the Invention] The catalyst for emission gas purification, and its manufacture method

[Claim(s)]

[Claim 1] The catalyst for emission gas purification characterized by becoming an oxide carrier and the platinum compound oxide layer formed in this oxide carrier surface more.

[Claim 2] The manufacture method of the catalyst for emission gas purification characterized by forming a platinum compound oxide layer in this oxide carrier surface by mixing an oxide carrier in the solution which dissolved ARUKOKISHIDO containing platinum, hydrolyzing this ARUKOKISHIDO, and subsequently calcinating.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the catalyst for emission gas purification, the catalyst for emission gas purification with which degradation of purification performance was prevented also in detailed hot lean atmosphere about the manufacture method, and its manufacture method.

[0002]

[Description of the Prior Art] The precious metals, such as platinum (Pt), rhodium (Rh), and palladium (Pd), are used as a catalyst ingredient, and these precious metals are supported by oxide carriers, such as alumina (Al_2O_3), and are used for the catalyst for emission gas purification arranged conventionally at exhaust air systems, such as a car. In order Pt is especially generous in resources compared with Rh and to show high catalyst activity compared with Pd, Pt is mainly used for the catalyst for emission gas purification for cars.

[0003] However, Pt oxidizes in hot lean atmosphere and there is a problem that surface area decreases with a sinter ring and catalyst activity falls remarkably. Moreover, since it is in improvement in engine performance in recent years, the increase in high speed operation, and the tendency for exhaust gas temperature to become still higher by strengthening of emission control etc. further, development of a means to control the sinter ring of Pt is called for strongly.

[0004] Then, the applicant for this patent has proposed the catalyst using Pt, a run TANOIDO element, or a perovskite type compound oxide with alkaline-earth metals in JP,S62-277150,A previously. According to this catalyst, since the heat deterioration of Pt and alloying are controlled compared with the conventional Pt / Al₂O₃ catalyst, endurance improves sharply. However, an exhaust gas temperature in recent years is very high, and is also set for the catalyst of an indication at JP,S62-277150,A. In the field over 900 degrees C, a perovskite type compound oxide will begin thermal cracking. Therefore, in order to cope with the further high temperature-ization of a future exhaust gas temperature, it is necessary to enable it to control the sinter ring of Pt also in a field which exceeds 1000 degrees C.

[0005] Then, invention-in-this-application persons inquired wholeheartedly, and have proposed the catalyst which mixes the powder and gamma-Al₂O₃ powder which consist of a Pt compound oxide containing one sort or two sorts or more of elements chosen from Pt, an alkaline-earth-elements element, or a periodic table 3A fellows element in JP,H10-358,A. According to this catalyst, since Pt is taken in during the crystal of a compound oxide and is stable, the high heat resistance of 1000 degrees C or more can be attained.

[0006]

[Problem to be solved by the invention] However, even if it is the catalyst of the indication to JP,H10-358,A, it is called for that it becomes clear that a certain amount of sinter ring arises in Pt compound oxide in hot lean atmosphere, and it controls the sinter ring of Pt further. This invention is made in view of such a situation, and it aims at being able to control the sinter ring of Pt further and considering it as the catalyst of high heat resistance.

[0007]

[Means for solving problem] There is the feature of the catalyst for emission gas purification of this invention which solves the above-mentioned technical problem in becoming an oxide carrier and Pt compound oxide layer formed in the oxide carrier surface more. Moreover, there is the optimal feature of the manufacture method of the catalyst for emission gas purification of this invention for manufacturing the above-mentioned catalyst in forming Pt compound oxide layer in an oxide carrier surface by mixing an oxide carrier in the solution which dissolved ARUKOKISHIDO containing Pt, hydrolyzing ARUKOKISHIDO, and subsequently calcinating.

[0008]

[Mode for carrying out the invention] [according to research of this invention persons / the sinter ring in a hot oxidization atmosphere of Pt compound oxide] When it was Pt compound oxide independent, it was the largest, when it mixed with an oxide carrier, that whose sinter ring decreases was still large, and when Pt compound oxide layer was formed in an oxide carrier surface filmy, it was found out that a sinter ring is controlled most. This invention is made based on this discovery.

[0009] That is, Pt compound oxide layer is formed in the oxide carrier surface with the catalyst for emission gas purification of this invention. Compared with the case where particle-like Pt compound oxide and an oxide carrier are mixed by this, the contact surface product of Pt compound oxide and a carrier becomes large, and it is thought that the sinter ring of Pt compound oxide is controlled. a kind chosen from alumina, silica, Chita Near, zirconia, a ceria, silica alumina, etc. as an oxide carrier -- or two or more sorts can be mixed and used. However, these oxides may react with the alkaline-earth metals in Pt compound oxide, the structure of Pt compound oxide may change, and catalyst activity may fall. Therefore, it is desirable for the oxide carrier itself to use the compound oxide containing alkaline-earth metals. Since the reaction of an oxide carrier and Pt compound oxide is inhibited by this, the endurance of a catalyst improves further.

[0010] It is desirable to use the compound oxide which consists of alumina, silica, Chita Near, zirconia, a ceria, silica alumina, etc. alkaline-earth metals, or a run TANOIDO element as such a compound oxide carrier. The desirable percentage is X:M=1 at a molar ratio, when aluminum, Si, Ti, Zr, Ce, etc. are expressed with M and alkaline-earth metals or a run TANOIDO element is expressed with X. : The range of 0.3-1:20 is desirable, and it is X:M=1. : Especially the range of 0.5-1:4 is desirable.

[0011] Although the specific surface area of an oxide carrier is so desirable that it is high, an important thing is that specific surface area does not change before and behind durability. If specific surface area does not change before and behind durability, effect sufficient also by a 15m²/g grade can be acquired. As a Pt compound oxide which constitutes Pt compound oxide layer, the compound oxide expressed with the following chemical formulae, for example is illustrated. (1) X₄PtO₆ ((X =Ca, Sr and Ba, Mg) 2) X'₂Pt₂O₇ Sc, La, and Pr make the Paik Roar system in this (X' = Sc, La, Pr) case. (3) SrX''PtO₆ These (X''=Co, nickel, Cu) One Sr of Sr₄PtO₆ is replaced. (4) Ba₂ZPtO₆ (Z =Pr, Ce) (5) What Cu, nickel, CO, Fe, etc. contained further can be preferably used for Ba₈Y₃Pt₄O_{17.5} and the above-mentioned Pt compound oxide. By decoding such a base metal, the endurance of a catalyst improves further. For example, if X illustrates what contains Cu further by Ba Ba₄CuPt₂O₉, Ba₂Y₂CuPtO₈, Ba₂Y₂Cu₂PtO₁₀, Ba₃Y₂Cu₂PtO₁₀, Ba_{1.3}Sr_{1.7}Y₂Cu₂PtO₁₀, Ba₂Ho₂CuPtO₈, Ba₂Ho₂Cu₂PtO₁₀, Ba₂Er₂CuPtO₈, Ba₃Er₂Cu₂PtO₁₀ etc. are mentioned.

[0012] As for the thickness of Pt compound oxide layer, it is desirable to be referred to as 0.05 micrometer or less, and especially its thing to consider as the thickness of a primary particle order is desirable. If the thickness of Pt compound oxide layer becomes thick, it is not desirable in order for the sinter ring between the secondary particles in Pt compound oxide layer to arise. Since the number of Pt ion which exists in the specific surface area and the surface of a catalyst is proportional with the catalyst for emission gas purification of this invention, specific surface area will be desirable, so that it is large. In order to enlarge specific surface area, it is desirable to form filmy Pt compound oxide layer in the surface using the detailed particle-like oxide carrier more than specific surface area of 15m²/g, as described above. Thus, in order to form filmy Pt compound oxide layer, an alkoxide process (sol-gel method) or a gaseous phase part solution can be used.

[0013] So, by the manufacture method of this invention for being stabilized and manufacturing the catalyst for emission gas purification of this invention, an oxide carrier is mixed in the solution which dissolved ARUKOKISHIDO which contains Pt first, and Pt compound oxide layer is formed in an oxide carrier surface by hydrolyzing ARUKOKISHIDO and subsequently calcinating. That is, by the manufacture method of this invention, Pt compound oxide layer is formed with the alkoxide process (sol-gel method). In an alkoxide process, an oxide is formed by calcinating the oxide precursor which ARUKOKISHIDO was dissolved in solvents, such as alcohol, it was considered as solution, and the oxide precursor which is solid hydroxide was deposited by hydrolysis and maturing, and subsequently deposited. Therefore, in the manufacture method of this invention, the hydroxide formed of hydrolysis and maturing deposits on the surface of the oxide carrier which lives together, and Pt compound oxide is formed in the surface of a particle-like carrier as a filmy Pt compound oxide layer by calcinating it.

[0014] The thing same as an oxide carrier used for the manufacture method of this invention as the oxide carrier used for the catalyst for emission gas purification of this invention can be used. namely, a kind chosen from alumina, silica, Chita Near, zirconia, a ceria, silica alumina, etc. -- or two or more sorts can be mixed and used. However, these oxides may react with the alkaline-earth metals in Pt compound oxide, the structure of Pt compound oxide may change, and catalyst activity may fall. Therefore, it is desirable for the oxide carrier itself to use the compound oxide containing alkaline-earth metals. Since the reaction of a carrier and Pt compound oxide is inhibited by this, the endurance of a catalyst improves further.

[0015] It is desirable to use the compound oxide which consists of alumina, silica, Chita Near, zirconia, a ceria, silica alumina, etc. alkaline-earth metals, or a run TANOIDO element as such a compound oxide carrier. The desirable percentage is X:M=1 at a molar ratio, when aluminum, Si, Ti, Zr, Ce, etc. are expressed with M and alkaline-earth metals or a run TANOIDO element is expressed with X. : The range of 0.3-1:20 is desirable, and it is X:M=1. : Especially the range of 0.5-1:4 is desirable.

[0016] Although the specific surface area of an oxide carrier is so desirable that it is high, an important thing is that specific surface area does not change before and behind durability. If specific surface area does not change before and behind durability, effect sufficient also by a 15m²/g grade can be acquired. moreover, as a solvent which dissolves ARUKOKISHIDO, it is independent about various alcohol -- it is -- although two or more kinds can be mixed and it can use, it is desirable to use ether and the mixed solvent of alcohol. A deposit of Pt acetylacetonato at the time of hydrolysis is controlled by this, and homogeneous gel is obtained. In addition, according to the kind and quantity of ARUKOKISHIDO to be used, various selections of the kind and the mixture ratio of ether and alcohol can be made.

[0017] the catalyst of obtained this invention -- a law -- it can pelletize by a method and practical use can be presented as a pellet catalyst. Moreover, a coat can be carried out to honeycomb carrier base materials, such as Caux Gela Ito and a product made from a metal, and practical use can also be presented as a monolithic catalyst. And an oxidation catalyst, a three-way catalyst, the catalyst for lean burn, the catalyst for diesels, and NO_x It can use for uses, such as occlusion and a returned type catalyst.

[0018]

[Working example] A work example and a comparative example explain this invention concretely hereafter. (Work example 1) 2-propanol 75g and 2-METOKISHI methanol 25g are mixed, and it is about $\text{Sr}(\text{OC}_3\text{H}_7)_2$ in this mixed solvent. 1.187g $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ 0.756g was supplied, it agitated at 70 degrees C under channeling back for 12 hours, and ARUKOKISHIDO solution was prepared.

[0019] On the other hand, 2-propanol 75g and 2-METOKISHI methanol 25g are mixed, and it is marketing in this mixed solvent. MgAl_2O_4 (specific surface area 40m²/g) In addition, 28.77g was agitated, it heated at 70 degrees C, and carrier dispersion liquid were prepared. Next, the 70-degree C above-mentioned ARUKOKISHIDO solution was added into 70-degree C carrier dispersion liquid, and it held at 70 degrees C, and agitated under channeling back for 1 hour. There nickel(CH_3COO) \cdot 2.4H₂O 478g added, and it held at 70 degrees C, agitated under channeling back for further 1 hour, and was considered as soil suspension.

[0020] Furthermore, it is deionized water, agitating the above-mentioned soil suspension. 0.208g was added gradually, and it held at 70 degrees C, and agitated under channeling back for 5 hours, and hydrolysis and maturing were performed. the obtained soil suspension -- ASUPIRETA 100 degrees C -- after degreasing -- further -- inside of N₂ it degreases at 300 degrees C -- it calcinated at 500 degree C for 3 hours, and the catalyst powder of this example was obtained. To this catalyst and 2OMgAl₄ carrier surface It is thought that Pt compound oxide layer expressed with $\text{Sr}_3\text{NiPtO}_6$ is formed and constituted, and the amount of support of Pt is 1.25 weight %.

[0021] (Work example 2) 2-propanol 75g and 2-METOKISHI methanol 25g are mixed, and it is about $\text{Sr}(\text{OC}_3\text{H}_7)_2$ 2 in this mixed solvent. 1.582g $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ 0.756g was supplied, it agitated at 70 degrees C under channeling back for 12 hours, and ARUKOKISHIDO solution was prepared. On the other hand, 2-propanol 75g and 2-METOKISHI methanol 25g are mixed, and it is marketing in this mixed solvent. MgAl_2O_4 (specific surface area 40m²/g) In addition, 28.77g was agitated, it heated at 70 degrees C, and carrier dispersion liquid were prepared.

[0022] Furthermore, it is deionized water, agitating the above-mentioned soil suspension. 0.208g was added gradually, and it held at 70 degrees C, and agitated under channeling back for 5 hours, and hydrolysis and maturing were performed. the obtained sediment -- ASUPIRETA 100 degrees C -- after degreasing -- further -- inside of N₂ it degreases at 300 degrees C -- it calcinated at 500 degree C for 3 hours, and the catalyst powder of this example was obtained. To this catalyst and 2OMgAl₄ carrier surface It is thought that Pt compound oxide layer expressed with Sr_4PtO_6 is formed and constituted, and the amount of support of Pt is 1.25 weight %.

[0023] (Comparative example 1) 313g dinitrodiammine Pt solution (it contains 0.2weight % as Pt) -- 50g gamma-Al₂O₃ powder (specific surface area 180m²/g) -- in addition, agitating, it is on bathing and moisture is evaporated -- 120 degree C -- one whole day and night -- after dryness and inside of the atmosphere It calcinated at 500 degrees C for 1 hour, and the catalyst powder of the comparative example 1 was obtained.

[0024] The catalyst of this comparative example 1 is considered that Pt is supported by high distribution even inside the fine pores of gamma-Al₂O₃ particles. (Comparative example 2) 2-propanol 1500g and 2-METOKISHI methanol 500g is mixed and it is about Sr(OC₃H₇)₂ 2 in this mixed solvent. 31.64g Pt(C₅H₇O₂)₂ 15.12g was supplied and it agitated at 70 degrees C under channeling back for 12 hours. Further 9.56g nickel(CH₃COO)₂·4H₂O was added, and it held at 70 degrees C, agitated under channeling back for 1 hour, and ARUKOKISHIDO solution was prepared.

[0025] Agitating this ARUKOKISHIDO solution, 4.16g of deionized water was added gradually, and it held at 70 degrees C, and agitated under channeling back for 5 hours, and hydrolysis and maturing were performed. and the obtained sediment -- ASUPIRETA 100 degrees C -- after degreasing -- further -- inside of N₂ it degreases at 300 degrees C -- it calcinates at 500 degree C for 3 hours -- Pt compound oxide powder expressed with Sr₃NiPtO₆ was prepared. Next, it is marketing to this Pt compound oxide powder. MgAl₂O₄ (specific surface area 40m²/g) In addition, it mixed well by the mortar and 28.77g of catalyst powder of the comparative example 2 was obtained. This catalyst and 2OMgAl₄ carrier Pt compound oxide expressed with Sr₃NiPtO₆ is mixed uniformly, it is constituted, and the amount of support of Pt is 1.25 weight %.

[0026] (Comparative example 3) 2-propanol 1500g and 2-METOKISHI methanol 500g is mixed and it is about Sr(OC₃H₇)₂ 2 in this mixed solvent. 23.74g Pt(C₅H₇O₂)₂ 15.12g was supplied, it agitated at 70 degrees C under channeling back for 12 hours, and ARUKOKISHIDO solution was prepared. Agitating this ARUKOKISHIDO solution, 4.16g of deionized water was added gradually, and it held at 70 degrees C, and agitated under channeling back for 5 hours, and hydrolysis and maturing were performed. and the obtained sediment -- ASUPIRETA 100 degrees C -- after degreasing -- further -- inside of N₂ it degreases at 300 degrees C -- it calcinates at 500 degree C for 3 hours -- Pt compound oxide powder expressed with Sr₄PtO₆ was prepared.

[0027] Next, it is marketing to this Pt compound oxide powder. MgAl₂O₄ (specific surface area 40m²/g) In addition, it mixed well by the mortar and 28.77g of catalyst powder of the comparative example 2 was obtained. This catalyst and 2OMgAl₄ carrier Pt compound oxide expressed with Sr₄PtO₆ is mixed uniformly, it is constituted, and the amount of support of Pt is 1.25 weight %. (Comparative example 4) 2-propanol 1500g and 2-METOKISHI methanol 500g is mixed and it is about Sr(OC₃H₇)₂ 2 in this mixed solvent. 31.64g Pt(C₅H₇O₂)₂ 15.12g was supplied and it agitated at 70 degrees C under channeling back for 12 hours. Further 9.56g nickel(CH₃COO)₂·4H₂O was added, and it held at 70 degrees C, agitated under channeling back for 1 hour, and ARUKOKISHIDO solution was prepared.

[0028] Agitating this ARUKOKISHIDO solution, 4.16g of deionized water was added gradually, and it held at 70 degrees C, and agitated under channeling back for 5 hours, and hydrolysis and maturing were performed. and the obtained sediment -- ASUPIRETA 100 degrees C -- after degreasing -- further -- inside of N₂ it degreases at 300 degrees C -- it calcinates at 500 degree C for 3 hours -- Pt compound oxide powder expressed with Sr₃NiPtO₆ was prepared, and it was considered as the catalyst powder of the comparative example 4. Consisting of only this catalyst and a Pt compound oxide expressed with Sr₃NiPtO₆, the amount of support of Pt is 1.25 weight %.

[0029] (Evaluation test) About the catalyst of a work example 1, a work example 2, the comparative example 2, the comparative example 3, and the comparative example 4, while observing the particle

with the scanning electron microscope, the element of the surface was analyzed by EDX. In addition, EDX analysis was conducted on the conditions shown in Table 1.

[0030]

[Table 1] ** ----- ** ----- **** accelerating voltage ** 20.00 kV **** probe current ** 0.22 nA A **** BG point degree of ** 3.63 keV and 8.50keV **** electron beam incidence angle ** -- 90.0 [degree] **** X-rays extraction angle ** -- 30.0 degree **** measuring time [**] -- 100 Although the catalyst of the second ****-----**-----** work examples 1 and 2 was uniform, two kinds of particles were observed by the catalyst of comparative examples 2 and 3.

[0031] The EDX analysis result of the catalyst of a work example 2 is shown in drawing 3. With the catalyst of the work example 2, as shown in drawing 3, Sr and Pt were detected in all the surfaces. On the other hand, with the catalyst of the comparative example 3, as shown in drawing 4, Sr and Pt were not detected at all by surface [most]. Furthermore, it is this portion since Sr and Pt were quantitatively detected from the surface of few portions by high concentration overwhelmingly in the catalyst of a comparative example 3 as shown in drawing 5. It is thought that it is the structure of Sr₄PtO₆. The phenomenon in which it was completely the same also in the case of the catalyst of a work example 1 and a comparative example 2 was observed.

[0032] With the catalyst of a comparative example 2 2OMgAl₄ carrier since it is clear that Pt compound oxide of the shape of a particle expressed with Sr₃NiPtO₆ is mixed uniformly, and is constituted As the above-mentioned analysis shows to drawing 1 with the catalyst of a work example 1, it is the shape of a particle. Pt compound oxide layer 2 expressed with Sr₃NiPtO₆ is formed in the whole surface of the MgAl₂O₄ carrier 1 surface. With the catalyst of a work example 2 On the whole surface of the MgAl₂O₄ carrier 1 surface It is clear that Pt compound oxide layer 2 expressed with Sr₄PtO₆ is formed. In addition, it is at drawing 1 here. Although 2OMgAl₄ carrier 1 was illustrated spherically typically, the surface may be a variant as long as it is a particle-like.

[0033] Next, by a normal temperature hydrostatic pressure press (CIP), the catalyst of a work example 1, a work example 2, and comparative examples 1-3 was pulverized after pressurization, and was fabricated to the pellet type of 1.0 to 1.7 mm, respectively. Each acquired pellet catalyst has been arranged to durability test equipment, and durable processing of 10 hours was performed at 1000 degrees C in the durable model gas (what added SO₂ to A/F=16 fairly) shown in Table 1.

[0034] Each pellet catalyst after durable processing Arrange 2.0g to a normal pressure circulation type reaction apparatus, respectively, and the valuation modeling gas (an equivalent for SUTOIKI) shown in Table 2 is supplied by 5l. the flux for /. The degree of catalyst floor temperature 500 degrees C reaches 300 degree C 350 degree C 400 degree C 450 degree C. The purification rate in the stationary state of C₃H₆ ingredient at 250 degrees C and NO ingredient was measured, respectively. In addition, the definition of a purification rate is expressed with the following formula. Purification rate = 100x {(concentration in the concentration-appearance gas in ON gas) concentration in /ON gas}

[0035]

[Effect of the Invention] That is, according to the catalyst for emission gas purification of this invention, the sinter ring of Pt can be controlled further, high purification performance is discovered also after the durable processing heated at 1000 degrees C, and it excels in heat resistance extremely. Moreover, according to the manufacture method of this invention, it is stabilized and the catalyst which has the above-mentioned outstanding heat resistance can be manufactured certainly.

[Brief Description of the Drawings]

[Drawing 1] It is the typical sectional view showing the structure of the catalyst for emission gas purification of one work example of this invention.

[Drawing 2] It is the explanatory view showing the mechanism of the sinter ring in the conventional catalyst for emission gas purification.

[Drawing 3] It is the EDX chart figure showing the ultimate analysis result on the surface of a catalyst of a work example 2.

[Drawing 4] It is the EDX chart figure showing the ultimate analysis result of the surface which occupies most catalysts of a comparative example 3.

[Drawing 5] It is the EDX chart figure of the catalyst of a comparative example 3 showing the ultimate analysis result of the surface of few portions overwhelmingly.

[Explanations of letters or numerals] 1: 2OMgAl4 carrier (particle-like carrier) 2: Pt compound oxide layer

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